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Tunable band gaps in silicene/MoS₂ heterobilayers

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Abstract

The geometric and electronic properties of silicene paired on MoS₂ substrate are studied systematically by using density functional theory with van der Waals correction. It is found that the nearly linear band dispersion can be preserved in the heterobilayers due to the weak interface interactions. Meanwhile, the band gap is opened because of the sublattice symmetry broken by the intrinsic interface dipole. Moreover, the band gap values could be effectively modulated under an external electric field. Therefore, a way is paved for silicene/MoS₂ heterobilayers as the candidate materials for logic circuits and photonic devices.

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Electronic supplementary information (ESI) available: Comparable band structures of pristine silicene and silicene/ MoS_2 heterobilayer without and with strain, the structures and lattice parameters for unstable configurations of heterobilayers.

1. Introduction

Silicene,¹ the Si counterpart of graphene, is a two-dimensional crystal with a hexagonal lattice structure. Experimentally, it has been synthesized successfully in forms of pristine monolayer on Ag surface,^{2, 3, 4} ZrB₂ thin films⁵ and Ir surface,⁶ Mg-doped sheets⁷ and free-standing Si multilayers.⁸ Since its discovery, it has triggered enormous interest in exploring the unique properties and potential applications. The electronic band structure of silicene is very similar to that of graphene: it is a zero-gap semi-metal with Dirac cones at Fermi energy $(E_{\rm F})^{9,10}$ Thus, the extremely high carrier mobility is expected from the linear energy dispersion relation near $E_{\rm F}$, and the intrinsic value for pristine silicene is theoretically estimated on the order of $10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.¹¹ When silicene is used as the channel, the transistor would own an ultrafast speed, making it able to operate in the THz frequency range.¹² Thus the fascinating electronic properties and compatibility with the existing electronics industry make silicene a promising material for high-speed switching devices. Moreover, several intriguing properties which are different from graphene can be brought into silicene. For instance, the quantum spin Hall effect can be observed in an experimentally accessible low temperature regime in silicene with a much higher spin-orbital band gap than graphene.^{13,14} The low-buckling of silicene¹⁵ facilitates the gap opening via applying the external electric field (F), ^{16,17,18} or pairing on a substrate.¹⁹ In addition, it is found that the stronger binding of metal adatoms to silicene,²⁰ high-sensitive silicene to NH₃, NO and NO₂ molecules²¹ and relatively low barriers for Li diffusion in silicene.²²

Due to the reactive nature of Si in silicene,^{20, 23} the existence of substrates could increase the structural stability.²⁴ Currently, most of the preparations of silicene are focused on the metallic substrates,^{4, 25} which are undesired in nanoelectronic devices. Moreover, the strong silicene-substrate interaction would destroy the Dirac cone of silicene and thus make the carrier mobility greatly reduce.⁵ Consequently, it is desirable to find a proper non-metallic substrate to accommodate silicene without disturbing its Dirac feature. Besides that, a sizable and tunable band gap (E_g) opened at the Dirac point is also highly expected towards the electronic applications.¹² Some semiconducting substrates have been proposed theoretically, such as BN²⁶ and GaS sheets,²⁷ SiC,²⁸ Si,²⁹ diamond³⁰ and ZnS surfaces³¹ for silicene-based nanoelectronic devices. Despite these achievements, there is no experimental evidence for these heterostructures.

Very recently, the Si single layer epitaxial grown on MoS₂ substrate was successfully synthesized with improved conductivity.³² It is known that bulk MoS₂ is a semiconductor with indirect bandgap (1.29 eV), whereas the MoS₂ monolayer is optically active with a direct E_g of about 1.90 eV.³³ Thus, MoS₂ would be used as the substrates with the added advantage of layered graphite-like structure with hexagonal atomic arrangement. Actually, the graphene absorbed on MoS₂ substrate has attracted extensive experimental and theoretical attention.^{34, 35, 36} However, the systematic analysis of the electronic properties of the heterobilayers (henceforth silicene/MoS₂) from the theoretical point of view is absent so far. Therefore, in the following, we investigate the structural and electronic properties of silicene/MoS₂ heterobilayers by

density functional theory (DFT) calculations with van der Waals (vdW) correction. We find that the interaction between silicene and MoS₂ substrate is weak, it is thus expected that the Dirac states are not perturbed in the heterobilayers. Moreover, a sizable E_g is opened in silicene/MoS₂ and the value is tunable under *F*.

2. Computational methods and models

The first-principle DFT calculations are performed within the DMol³ code.^{37,38} The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) is utilized as the exchange-correlation functional.³⁹ Because the weak interactions are not well described by the standard PBE functional, the DFT-D (D stands for dispersion) approach within the Grimme scheme is adopted for the vdW correction.⁴⁰ DFT Semi-core Pseudopots (DSPP), which induce some degree of relativistic correction into the core, are used for the core treatment. Moreover, double numerical atomic orbital plus polarization is chosen as the basic set with the global orbital cutoff of 4.6 Å. The k-point is set to $9 \times 9 \times 1$ for structural optimizations and $16 \times 16 \times 1$ for electronic properties calculations, and the smearing value is 0.005 Ha (1 Ha = 27.2114 eV). The convergence tolerance of energy, maximum force, and maximum displacement are set to 1.0×10^{-5} Ha, 0.002 Ha/Å and 0.005 Å, respectively. A large vacuum of 60 Å is used to prevent the interaction and artificial dipole moment effects from neighboring cells in the direction normal to the silicene surface. The F is applied in the direction perpendicular to the heterobilayer plane from -1.0 to 1.0 V/Å, and then geometry relaxation is carried out. This method for applying the electric field is similar with the previous report.¹⁶ The part about plane-averaged electron density and

electron density difference is calculated in CASTEP code,⁴¹ with a plane-wave kinetic energy cutoff of 290 eV. It is believed that the numerical basic sets implemented in DMol³ could minimize or even eliminate basis set superposition error (BSSE) compared with the Gaussian basis sets.⁴² Since DMol³ uses the exact DFT spherical atomic orbitals, the molecules can be dissociated exactly to its constituent atoms. Consequently, the corrections of BSSE are not considered here.

The lattice parameters of pristine silicene and MoS₂ monolayer are 3.82 and 3.13 Å, respectively.⁴³ Note that the matched structure usually forms when the mismatch between lattice constants is small.⁴⁴ Being similar with the modeling methods of graphene/MoS₂ heterostructures,^{35, 36} we impose a commensurability condition between the silicene and MoS₂ monolayer, where a 4×4 lateral periodicity of silicene and 5 \times 5 lateral periodicity of the MoS₂ monolayer are employed, resulting in a mismatch of around 2.42%. We choose the lattice constant of MoS₂ substrate (15.65 Å), and scale the in-plane lattice constant of silicene. Our test computations show that for the pristine silicene the elongation of lattice constant by 2.42% has little effect on $E_{\rm g}$ because the sublattice symmetry is still kept (see Fig. S1 (a) in ESI), which is consistent with the previous results.⁴⁵ We also consider other matching procedure for the heterobilayers, such as adopting the lattice constant of pristine silicene (15.28 Å), and find no noticeable differences for the band structures (see Fig. S1 (b) in ESI). We have also studied substrate of MoS₂ with varying thickness. It turns out that for the heterostructures with vdW interlayer interaction, the thickness of substrate hardly influence on the electronic states near $E_{\rm E}$.⁴⁶ Thus, in the following, we will focus on

the case of MoS₂ monolayer.

To quantitatively characterize the interface binding properties, the binding energy (E_b) between the silicene and MoS₂ monolayer is calculated as,

$$E_{\rm b} = E_{\rm total} - E_{\rm silicene} - E_{\rm MoS2},\tag{1}$$

where E_{total} , E_{silicene} and E_{MoS2} are energies of the composite, free-standing silicene and pristine MoS₂ monolayer, respectively. Based on this definition, a larger E_{b} value stands for the stronger interface binding.

3. Results and discussion

For the silicene/MoS₂ hybrids, six representative configurations are considered and the corresponding structural parameters are calculated (see Fig. S2 and Table S1 in ESI). The structural parameters and E_b for different patterns are similar, which is in agreement with the graphene/MoS₂ heterobilayers.³⁵ Thus, in the following, we only consider the most stable configuration in Fig. 1, where in a supercell one Si atom is directly above one S atom and one Si atom is located above the hollow site of MoS₂ hexagon. E_b is 120.32 meV per Si atom, which is similar with that for silicene/GaS (126 meV per Si atom) within plane-wave basis set.²⁷ It denotes our calculations for E_b are reliable. The interlayer distance *d* as labeled in Fig. 1 is 2.93 Å. The *d* value is much larger than the sum of covalent radii of Si and S atoms, which means that the Si atoms of silicene and S atoms of MoS₂ are beyond bonding range. The buckled distance in silicene (Δ) is 0.56 Å, being a little larger than that in pure silicene (0.44 Å),^{9,15} suggesting the slight structural distortion in silicene is induced by the substrate. Thus, silicene is found to interact weakly with the MoS₂ monolayer.

It was reported that the electronic properties of graphene-related materials would be modulated notably by the weak interlayer interactions.^{29, 47} To reveal this effect on silicene, the band structure of silicene/MoS₂ is calculated in Fig. 2(c). As a comparison, the band structures of pristine silicene and MoS₂ monolayer are first calculated in Figs. 2(a) and 2(b), respectively. For MoS₂ monolayer, $E_g = 1.84$ eV, being similar with the experimental results.³³ Obviously, the band structure of silicene/MoS₂ seems to be a simple sum of those of each constituent, as expected on the basis of the relatively weak interlayer interactions. Remarkably, the curvature of band dispersion around the Dirac point of silicene/MoS₂ is almost linear, suggesting the carrier effective mass and consequently the high carrier mobility is hardly influenced by the MoS₂ substrate.^{26, 28, 29} In order to see the states near $E_{\rm F}$, the partial density of states (PDOS) of the separated silicene and MoS₂ from the heterobilayer are plotted in Fig. 2(d). It is found that the states of silicene/MoS₂ near E_F are dominated by π and π^* bands in silicene, denoting that the electronic and transport behaviors of the hybrid structure are mainly determined by silicene. More importantly, a considerable E_g of 70 meV is opened at K-point, which is more pronounced than the room temperature thermal scale (26 meV). It denotes that the on-off current ratio in logical devices would largely improve. The opened E_g in silicene/MoS₂ is much larger than that in graphene/MoS₂ (nearly zero),³⁵ denoting the opening E_g is much easier for silicene. Since the presence of a finite E_g without degrading the electronic properties of silicene is highly expected, 48 the MoS_2 is a suitable choice as a substrate for silicene-related electronic devices.

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In order to gain more insights into the opened E_g of silicene/MoS₂, we calculate the plane-integrated electron density difference $\Delta \rho = \rho_{\text{total}} - \rho_{\text{silicene}} - \rho_{\text{MoS2}}$ (ρ_{total} , ρ_{silicene} and ρ_{MoS2} are the plane-averaged electron density of silicene/MoS₂, silicene and MoS₂, respectively) to visualize the electron redistribution upon the formation of interface in Fig. 3. The notable electron rearrangement localizes at the interface and this behavior is visually revealed in the inset of Fig. 3. Clearly, electrons are depleted on the silicene side (yellow area), while piled up on MoS₂ side (blue area). Moreover, electron orbital overlap between silicene and MoS₂ layer is observed. This electron redistribution occurred at the interface often leads to the intrinsic interface dipole and it is quite general for a heterostructure with vdW interlayer interaction.^{46,49}

The flowing direction of electrons can be judged simply by the related work function (*W*). Let *W* be the energy barrier to extract an electron from the position of $E_{\rm F}$ to the vacuum level. For pristine silicene, *W* value calculated is 4.79 eV, being close to other literature data.^{50, 51} While for MoS₂ monolayer, *W* = 5.36 eV, which is 0.57 eV larger than that of silicene. Thus, the electrons may transfer from silicene to MoS₂. The definitive quantities for the electrons injection into MoS₂ are the energy level disposition between the ionization potential and electron affinity potential of the MoS₂, i.e., the valence band maximum (VBM) and conduction band minimum (CBM), and the *W* of silicene. As shown the schematic map in Fig. 4, for our system, the $E_{\rm F}$ of silicene lies between the VBM and CBM of MoS₂ monolayer. According to the integer charge transfer model,^{52, 53} the charge transfer is negligible, and the so-called vacuum level alignment holds for such type of interface.⁵⁴ Thus, the electrical

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Moreover, the average Mulliken population of A and B sublattices in silicene (e_A and e_B) are 0.074 and -0.056 e, respectively, which means the sublattice symmetry in silicene is broken. The sublattice asymmetry can be also reflected in Fig. 3 where the electron density around the A and B sublattices in silicene distributes unequally. It is because that the Coulomb fields felt by the A and B sublattices in a buckled structure are different, resulting to the two sublattices no longer equivalent. Thus, according to a tight-binding model, a gap at K-point is opened.⁵⁶ It is noted that although the Mulliken population analysis is rough and incapable of taking the charge's spatial distribution into account, the e_A and e_B can be used here to reflect the asymmetry between the two sublattices in silicene.

Actually, as the mechanism of E_g opening for silicene/MoS₂ is induced by the intrinsic interface dipole, an external electric field would continuously modulate the electron redistribution at the interface and thus eventually tune the E_g , as reported for the free-standing silicene and silicene/BN hybrid.^{16,17} Thus, to resolve this proposal, we introduce an external electric field to silicene/MoS₂ heterobilayers. The electric field direction is shown in the inset of Fig. 5 (a) where the positive direction points from MoS₂ to silicene. Under *F* the structure modulations of heterobilayers are only a little. When *F* changes from -1.0 to 1.0 V/Å, the Δ and *d* values have the small oscillations between 0.56 to 0.60 Å and 2.91 to 2.95 Å, respectively. Thus, it is found that the effect of structural modification on E_g is also slight (within 8 meV).

However, *F* has a remarkable impact on the electronic properties of silicene/MoS₂ heterobilayers. The E_g value as a function of *F* is displayed in Fig. 5 (a). Under a positive *F*, E_g monotonously enlarges up to 191 meV. When a negative *F* is applied, E_g first decreases and disappears under F = -0.5 V/Å, then it progressively increases to 75 meV under F = -1.0 V/Å. Clearly, the E_g value is nearly linear dependent on *F*, the slope of which is 0.15 e·Å, being slightly smaller than the value for free-standing silicene (0.17 e·Å).¹⁶ It is concluded that the combined effect of substrate and *F* on E_g for silicene/MoS₂ is almost a simple summation of the separated effects. The linear relation of E_g on *F* was also reported for silicene/BN and silicene/GaS hybrids.^{16, 27} Note that the high electric breakdown of silicene and MoS₂ layers allows the application of large electric bias.^{16, 57}

In order to understand the tunable E_g under F, Fig. 5 (b) displays the e_A and e_B , and average Mulliken population in silicene as a function of F. When F is applied in the positive direction, the negative electrons are "pushed" from silicene to MoS₂, thus the silicene is more positive charged with F, and then the dipole at the interface enhances. When F reaches 1.0 V/Å, silicene loses 0.044 e per Si atom. When F is applied in the negative direction, the transferred direction of electrons is from MoS₂ to silicene. Thus, the charge of silicene first decreases to zero at F = -0.3 V/Å. With further increase of F, silicene is no longer positive charged; on the contrary, silicene is more and more negative charged, and the value reaches -0.023 e at F = -1.0 V/Å. At this time, the negative F compensates the intrinsic dipole at the interface first, and

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then the reversed dipole increases. Meanwhile, e_A monotonously increases (reduces) under the positive (negative) F, while the variation of e_B is opposite on e_A . Namely, the e_A and e_B deviate from each other under a positive F, when a negative F is applied, they approach each other first until $e_A = e_B$, and then deviate each other. Consequently, a positive F increases the broken-symmetry between the two sublattices, leading to an increased E_g . While a negative F reduces the asymmetry first and then increases it thus makes E_g reduce first and then increase.

Moreover, the magnitude of E_g in silicene/MoS₂ is robust in stacking (see Table S1 in ESI), which may bring convenience for experimental preparation and device integration. The similar modulation of E_g in response to F as stable pattern holds true for other patterns, thus, depending on the direction and strength of F, E_g of silicene/MoS₂ heterobilayer can be efficiently tuned. Consequently, the hybrid structures of silicene/MoS₂ provide a promising candidate for fabricating logic circuits and photonic devices. Finally, we must point out that the experiments for silicene/MoS₂ heterostructures were carried out in an ultra-high vacuum condision.³² Fortunately, the theoretical results predicted that the arrangements of silicene between graphene or BN layers were proposed to synthesize silicene with electronic properties decoupled from the substrate, which were stable well above room temperature.^{16, 58} This is may be a possible direction for the experimental fabrication and applications of silicene-related materials.

4. Conclusions

In conclusion, our DFT calculations with vdW correction demonstrate that the

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structural and electronic properties of silicene/MoS₂ heterobilayers are fairly robust to stacking order. The interaction of silicene and substrate is weak, which ensures the high carrier mobility largely preserved. Moreover, a sizable E_g is induced by the intrinsic interface dipole, which breaks the symmetry between the two sublattices in silicene. Under a vertical *F*, the heterobilayer exhibits a continuously tunable E_g . Thus, the silicene/MoS₂ heterobilayers are potential candidates for the high performance nanoelectronic devices.

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1. G. G. Guzm-Verri and L. C. Lew Yan Voon, *Phys. Rev. B*, 2007, **76**, 075131.

2. P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet and G. Le Lay, *Phys. Rev. Lett.*, 2012, **108**, 155501.

3. B. Aufray, A. Kara, S. Vizzini, H. Oughaddou, C. Leandri, B. Ealet and G. Le Lay, *Appl. Phys. Lett.*, 2010, **96**, 183102.

4. A. Kara, H. Enriquez, A. P. Seitsonen, L. C. Lew Yan Voon, S. Vizzini, B. Aufray and H. Oughaddou, *Surf. Sci. Rep.*, 2012, **67**, 1.

5. A. Fleurence, R. Friedlein, T. Ozaki, H. Kawai, Y. Wang and Y. Yamada-Takamura, *Phys. Rev. Lett.*, 2012, **108**, 245501.

6. L. Meng, Y. Wang, L. Zhang, S. Du, R. Wu, L. Li, Y. Zhang, G. Li, H. Zhou, W. A. Hofer and H.-J. Gao, *Nano Lett.*, 2013, **13**, 685.

7. H. Nakano, T. Mitsuoka, M. Harada, K. Horibuchi, H. Nozaki, N. Takahashi, T. Nonaka, Y. Seno and H. Nakamura, *Angew. Chem. Int. Ed.*, 2006, **45**, 6303.

8. U. Kim, I. Kim, Y. Park, K.-Y. Lee, S.-Y. Yim, J.-G. Park, H.-G. Ahn, S.-H. Park and H.-J. Choi, *ACS Nano*, 2011, **5**, 2176.

9. S. Cahangirov, M. Topsakal, E. Akturk, H. Sahin and S. Ciraci, Phys. Rev. Lett., 2009, 102, 236804.

- 10. D. Jose and A. Datta, Acc. Chem. Res., 2014, 47, 593.
- 11. Z.-G. Shao, X.-S. Ye, L. Yang and C.-L. Wang, J. Appl. Phys., 2013, 114, 093712.
- 12. Y. F. Zhu, Q. Q. Dai, M. Zhao and Q. Jiang, Sci. Rep., 2013, 3, 1524.
- 13. C.-C. Liu, W. Feng and Y. Yao, *Phys. Rev. Lett.*, 2011, **107**, 076802.
- 14. M. Tahir and U. Schwingenschlögl, Sci. Rep., 2013, 3, 1075.
- 15. D. Jose and A. Datta, J. Phys. Chem. C, 2012, 116, 24639.
- 16. Z. Ni, Q. Liu, K. Tang, J. Zheng, J. Zhou, R. Qin, Z. Gao, D. Yu and J. Lu, Nano Lett., 2012, 12, 113.
- 17. N. D. Drummond, V. Zólyomi and V. I. Fal'ko, Phys. Rev. B, 2012, 85, 075423.
- 18. E. Motohiko, New J. Phys., 2012, 14, 033003.
- 19. W.-F. Tsai, C.-Y. Huang, T.-R. Chang, H. Lin, H.-T. Jeng and A. Bansil, Nat. Commun., 2013, 4, 1500.
- 20. X. Lin and J. Ni, Phys. Rev. B, 2012, 86, 075440.
- 21. W. Hu, N. Xia, X. Wu, Z. Li and J. Yang, Phys. Chem. Chem. Phys., 2014, DOI: 10.1039/C3CP55250K.
- 22. G. A. Tritsaris, E. Kaxiras, S. Meng and E. Wang, Nano Lett., 2013, 13, 2258.
- 23. N. Gao, W. T. Zheng and Q. Jiang, Phys. Chem. Chem. Phys., 2012, 14, 257.
- 24. J. Gao and J. Zhao, Sci. Rep., 2012, 2, 861.
- 25. W. Hu, Z. Li and J. Yang, J. Chem. Phys., 2013, 139, 154704.
- 26. Z.-X. Guo, S. Furuya, J.-i. Iwata and A. Oshiyama, Phys. Rev. B, 2013, 87, 235435.
- 27. Y. Ding and Y. Wang, Appl. Phys. Lett., 2013, 103, 043114.
- 28. H. Liu, J. Gao and J. Zhao, J Phys. Chem. C, 2013, 117, 10353.
- 29. Y. Li and Z. Chen, J. Phys. Chem. Lett., 2012, 4, 269.
- 30. K. Chen, X. Wan and J. Xu, J Mater. Chem. C, 2013, 1, 4869.

31. M. Houssa, B. van den Broek, E. Scalise, G. Pourtois, V. V. Afanas'ev and A. Stesmans, *Phys. Chem. Chem. Phys.*, 2013, **15**, 3702.

32. D. Chiappe, E. Scalise, E. Cinquanta, C. Grazianetti, B. van den Broek, M. Fanciulli, M. Houssa and A. Molle, *Adv. Mater.*, 2013, DOI: 10.1002/adma.201304783.

- 33. K. F. Mak, C. Lee, J. Hone, J. Shan and T. F. Heinz, Phys. Rev. Lett., 2010, 105, 136805.
- 34. K. Chang and W. Chen, *Chem. Commun.*, 2011, **47**, 4252.

35. Y. Ma, Y. Dai, M. Guo, C. Niu and B. Huang, *Nanoscale*, 2011, **3**, 3883.

36. X. D. Li, S. Yu, S. Q. Wu, Y. H. Wen, S. Zhou and Z. Z. Zhu, J. Phys. Chem. C, 2013, 117, 15347.

37. B. Delley, J. Chem. Phys., 1990, 92, 508.

38. B. Delley, J. Chem. Phys., 2000, 113, 7756.

39. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

40. S. Grimme, J. Comput. Chem., 2006, 27, 1787.

41. M. D. Segall, Philip J. D. Lindan, M. J. Probert, C. J. Pichard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys.: Condens. Matter*, 2002, **14**, 2717.

42. Y. Inada and H. Orita, J. Comput. Chem., 2008, 29, 225.

43. N. Gao, J. Li and Q. Jiang, Chem. Phys. Lett., 2014, 592, 222.

44. M. Gao, Y. Pan, C. Zhang, H. Hu, R. Yang, H. Lu, J. Cai, S. Du, F. Liu and H. J. Gao, *Appl. Phys. Lett.*, 2010, **96**, 053109.

45. T. P. Kaloni, Y. C. Cheng and U. Schwingenschlogl, J. Appl. Phys., 2013, 113, 104305.

46. X. F. Chen, Y. F. Zhu and Q. Jiang, *RSC Adv.*, 2014, **4**, 4146.

47. Y. Li, F. Li and Z. Chen, J. Am. Chem. Soc., 2012, 134, 11269.

48. R. Quhe, R. Fei, Q. Liu, J. Zheng, H. Li, C. Xu, Z. Ni, Y. Wang, D. Yu, Z. Gao and J. Lu, *Sci. Rep.*, 2012, **2**, 853.

49. T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard and D. C. Langreth, *Phys. Rev. B*, 2007, **76**, 125112.

50. H. Sahin and F. M. Peeters, Phys. Rev. B, 2013, 87, 085423.

51. R. Qin, C.-H. Wang, W. Zhu and Y. Zhang, *AIP Adv.*, 2012, **2**, 022159.

52. L. Chen, L. Wang, Z. Shuai and D. Beljonne, J. Phys. Chem. Lett., 2013, 4, 2158.

53. W. Hu, Z. Li and J. Yang, J. Chem. Phys., 2013, 138, 124706.

54. T. Hu and I. C. Gerber, J. Phys. Chem. C, 2013, 117, 2411.

55. E. Kan, H. Ren, F. Wu, Z. Li, R. Lu, C. Xiao, K. Deng and J. Yang, J Phys. Chem. C, 2012, 116, 3142.

56. J. B. Oostinga, H. B. Heersche, X. Liu, A. F. Morpurgo and L. M. K. Vandersypen, *Nat. Mater.*, 2007, **7**, 151.

57. D. Lembke and A. Kis, ACS Nano, 2012, 6, 10070.

58. M. Neek-Amal, A. Sadeghi, G. R. Berdiyorov and F. M. Peeters, *Appl. Phys. Lett.*, 2013, **103**, 261904.

Captions

Fig. 1 (a) Top and (b) side views of stable silicene/MoS₂ configurations. The yellow, blue, khaki and brown balls denote S, Mo, A and B sublattices of Si atoms in silicene, respectively. The buckled value in silicene and the distance between the two layers is labeled. The supercell is represented by the green lines.

Fig. 2 Band structures of (a) free-standing silicene, (b) isolated MoS₂ monolayer and (c) silicene/MoS₂ heterobilayer. (d) PDOS for separated silicene and MoS₂ from the heterobilayer. The Fermi energy is set to zero.

Fig. 3 Plane-integrated electron density difference $\Delta\rho$ for silicene/MoS₂. The vertical dashed lines indicate the location of each layer for a given composite system. The inset is the 3D isosurface of electron density difference, the blue and yellow areas represent electron accumulation and depletion, respectively, and the isosurface value is ±0.0025 electrons/Å³.

Fig. 4 Schematic drawing of the energy level disposition for the pristine MoS₂ monolayer and silicene.

Fig. 5 (a) E_g and (b) Mulliken charge of A sublattice, B sublattice and silicene as a function of *F* for silicene/MoS₂. The inset of Fig. 5 (a) is sketch map of *F* direction.

Fig. 1











Fig. 4





